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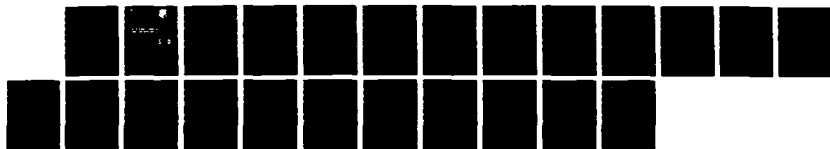
THE VPE-HYDRIDE TECHNIQUE WITH ALLOY SOURCE;
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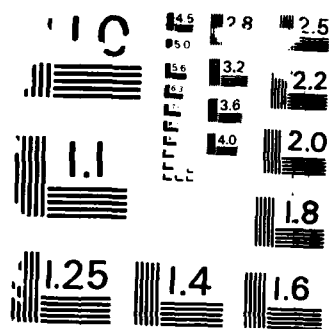
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In-House Report
November 1987

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***THE VPE-HYDRIDE TECHNIQUE WITH ALLOY
SOURCE; EQUILIBRIUM ANALYSIS***

Kenneth P. Quinlan

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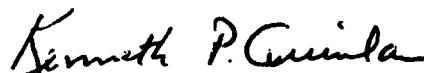
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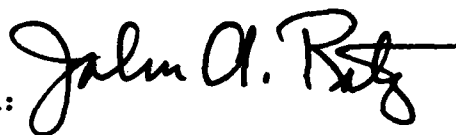
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<p>An equilibrium analysis of the VPE-hydride technique using an alloy source has been completed with the analysis method of Quinlan. Results of the analysis are in close agreement with the experimental findings of other investigators. The compositions of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ are dependent on the alloy compositions, and the initial partial pressures of hydrogen chloride and arsenic. The indium content of the ternaries increases with increasing arsenic pressures below 1.0×10^{-3} atm and remains constant above this value. The analysis indicates that the lattice matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ can continually be prepared from the same alloy by changing the initial partial pressures of hydrogen chloride.</p>					
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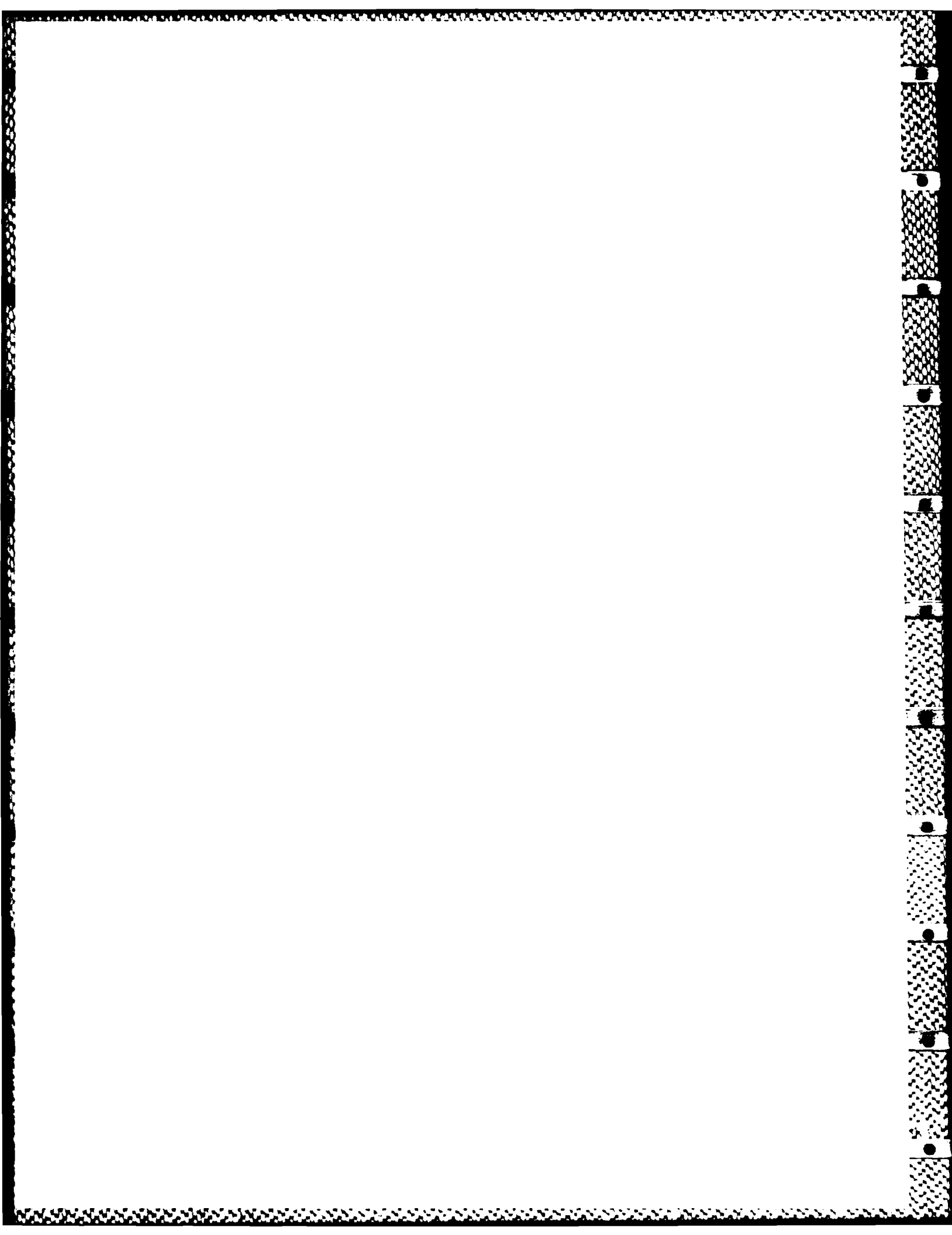
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The VPE-Hydride Technique With Alloy Source; Equilibrium Analysis

1. INTRODUCTION

$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is an extremely important material in the areas of optoelectronic and microwave devices, for example, bipolar transistors,¹ MODFET's,² MISFET's,³ photodiodes,⁴ and lasers.⁵ Epitaxial layers of this ternary have been grown by the various techniques: MOCVD,⁶ MBE,⁷ LPE,⁸ VPE-chloride,⁹ VPE-hydride,¹⁰ and CBE.¹¹ The VPE-hydride method has many advantages and these have been adequately described by Olsen and Zamerowski.¹² Macrander and Strege¹³ have reported the growth of a highly perfect $\text{Ga}_x\text{In}_{1-x}\text{As}$ epitaxial layer with the VPE-hydride technique.

The VPE-hydride process for the preparation of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ requires a quartz reactor with two separate compartments, one for each metal, namely, indium and gallium. A series of studies¹⁴⁻¹⁷ have investigated the use of an alloy source to replace the double-barrel reactor. Proponents of the use of the alloy source have indicated an additional advantage where the requirement for the precise control of the two hydrogen chloride flow rates over the metals is removed. These studies showed that high quality epitaxial layers of $\text{In}_x\text{Ga}_{1-x}\text{As}$ can be prepared with

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(Due to the large number of References cited above, they will not be listed here. See References, page 15.)

the alloy source. However, different investigators reported different alloy compositions for the preparation of the lattice matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

Various equilibrium analyses of the deposition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ by the VPE techniques have been reported.¹⁸⁻²² The only reported equilibrium analyses of the VPE-hydride technique using an alloy source are those of Jacobs et al²³ and Kajiyama.²⁰ I have recently developed a new and simple method²⁴ where the equilibrium expression can be used directly to analyze the VPE-hydride system with the two metal sources. This new method has been applied in this report to the VPE-hydride technique with the alloy source. Results of the study explain the previous experimental data and indicates the effect of varying the alloy composition, the partial pressures of hydrogen chloride and arsine on the composition of the ternaries. The equilibrium analysis also shows that the same alloy source can continually be used to produce the lattice matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

2. EQUILIBRIUM ANALYSIS

The equilibrium analysis of the alloy system was accomplished with the method developed in Reference 24. The equation for the deposition of the ternary, $\text{In}_x\text{Ga}_{1-x}\text{As}$, is



18. Nagai, H., Shibata, T., and Okamoto, H. (1971) Thermodynamical analysis for the vapor growth of $\text{Ga}_x\text{In}_{1-x}\text{As}$ crystals, Japan. J. Appl. Phys. 10:1337.
19. Minagawa, S., Seki, H., and Eguchi, H. (1972) Thermodynamic calculation for the vapor growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$: the In-Ga-As-Cl-H system, Japan. J. Appl. Phys. 11:855.
20. Kajiyama, K. (1976) Vapor pressure dependence of the relative composition of III-V mixed crystals in vapor phase epitaxy, J. Electrochem. Soc. 123:423.
21. Nagai, H. (1979) A simple analysis of vapor phase growth; citing an instance of $\text{Ga}_x\text{In}_{1-x}\text{As}$, J. Electrochem. Soc. 126:1400.
22. Jacobs, K., Simon, I., Bugge, F., and Butter, E. (1984) A simple method for the calculation of the composition of the VPE grown $\text{Ga}_x\text{In}_{1-x}\text{As}$ as a function of growth parameters, J. Cryst. Growth 69:155.
23. Jacobs, K., Bugge, F., and Simon, I. (1986) Vapour phase epitaxy of $\text{Ga}_x\text{In}_{1-x}\text{As}$ in the Ga-In-HCl-AsH₃H₂ system using a mixed Ga/In source, Cryst. Res. Technol. 21:3.
24. Quinlan, K. P. (1987) Equilibrium analysis of the deposition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ by the VPE-hydride technique; method to predict the composition of the ternary, J. Cryst. Growth 87:319.

The equilibrium constant for the deposition reaction is

$$K = \frac{P_{\text{HCl}}}{P_{\text{InCl}}^x P_{\text{GaCl}}^{1-x} P_{\text{As}_4}^{1/4} P_{\text{H}_2}^{1/2}} \quad (2)$$

where the P 's represents the equilibrium partial pressures. In Eq. (2) K is the product of the equilibrium constants for the deposition of the binaries, InAs and GaAs, and the activity of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ is taken as one. The material balances of the reactants and products in Eq. (1) are depicted in the following relations:

$$P_{\text{HCl}} = P'_{\text{HCl}} + P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}} \quad (3)$$

where P'_{HCl} is the partial pressure of the residual hydrogen chloride that remains after the reaction of HCl with the metals indium and gallium. $P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ is equivalent to the amount of HCl formed in reaction 1. $P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ is the amount of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited expressed in equivalent atmospheres. The amount of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited is determined from the linear relationship given in Figure 4 of Reference 24, where $P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ is plotted as a function of P_{As_4} . $P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ has been found to be constant in the region where x varies from 0.5 to 0.6 at various P_{As_4} values.

$$P_{\text{InCl}}^x = (P_{\text{InCl}}^{\circ} - xP^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^x, \quad (4)$$

$$P_{\text{GaCl}}^{1-x} = (P_{\text{GaCl}}^{\circ} - (1-x)P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1-x}, \quad (5)$$

$$P_{\text{As}_4}^{1/4} = (P_{\text{As}_4}^{\circ} - \frac{1}{4}P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1/4}, \quad (6)$$

where P° 's are the initial partial pressures.

The determinations of x and $1-x$, the mole fractions of InAs and GaAs in $\text{In}_x\text{Ga}_{1-x}\text{As}$, respectively, are achieved with Eq. (7) by a simple iteration:

$$\begin{aligned}
K &= (P'_{\text{HCl}} + P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}}) \\
&\times [(P^\circ_{\text{InCl}} - xP^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^x \\
&\times (P^\circ_{\text{GaCl}} - (1-x)P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1-x} \times (P^\circ_{\text{As}_4} - \frac{1}{4} P^*_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1/4} P_{\text{H}_2}^{1/2}]^{-1}
\end{aligned} \tag{7}$$

where K ($K_{\text{InAs}} \cdot K_{\text{GaAs}}$) is determined for the derived thermodynamic relationships of Jacobs et al.²² The value used for P_{H_2} is the initial partial pressure of hydrogen and $P_{\text{As}_4}^\circ$ is equal to $\frac{1}{4} P_{\text{AsH}_3}^\circ$. P_{InCl}° and P_{GaCl}° which result from the reaction of HCl with the alloy source are determined by the method described in the following paragraphs.

The fractions of the initial partial pressure of hydrogen chloride, P_{HCl}° , reacting with each metal in the alloy source are the products of P_{HCl}° times the activity fraction of each metal, namely Eqs. (8) and (9),

$$P_{\text{HCl(In)}}^\circ = P_{\text{HCl}}^\circ \frac{a_{\text{In}}}{a_{\text{In}} + a_{\text{Ga}}} \tag{8}$$

$$P_{\text{HCl(Ga)}}^\circ = P_{\text{HCl}}^\circ \frac{a_{\text{Ga}}}{a_{\text{In}} + a_{\text{Ga}}} \tag{9}$$

where a is the activity. The activities of indium and gallium in the alloy are determined from the standard Eqs. (10) and (11),

$$a_{\text{In}} = \gamma_{\text{In}} N_{\text{In}} \tag{10}$$

$$a_{\text{Ga}} = \gamma_{\text{Ga}} N_{\text{Ga}} \tag{11}$$

where γ and N are the activity coefficient and mole fraction, respectively. The activity coefficients are calculated from the Eqs. (12) and (13) as presented by Panish and Ilegems:²⁵

25. Panish, M. B., and Ilegems, M. (1972) Phase equilibria in ternary III-V systems, in Progress in Solid State Chemistry, Vol. 7, H Reiss and J. O. McCaldin, Editors, p. 53, Pergamon Press, New York.

$$\gamma_{\text{In}} = \exp \frac{\alpha}{RT} (1 - N_{\text{In}})^2 \quad (12)$$

$$\gamma_{\text{Ga}} = \exp \frac{\alpha}{RT} (N_{\text{In}})^2 \quad (13)$$

where α is the interaction parameter whose value is taken as 1060 cal/mole.²⁵ The initial partial pressures of the III monochlorides (P_{InCl}° and P_{GaCl}°) are then calculated from the following equilibrium equations:

$$K_{\text{InCl}} = \frac{P_{\text{InCl}}^\circ \cdot P_{\text{H}_2}^{1/2}}{a_{\text{In}} \cdot P_{\text{HCl(In)}}} \quad (14)$$

$$K_{\text{GaCl}} = \frac{P_{\text{GaCl}}^\circ \cdot P_{\text{H}_2}^{1/2}}{a_{\text{Ga}} \cdot P_{\text{HCl(Ga)}}} \quad (15)$$

where the K values for Eqs. (14) and (15) were calculated using the thermodynamic data of Seki et al.²⁶ and Kirwan,²⁷ respectively.

The residual hydrogen chloride partial pressure (P_{HCl}') in Eqs. (3) and (7) is the sum of the differences between the $P_{\text{HCl(III)}}^\circ$'s and the $P_{\text{III Cl}}^\circ$'s.

26. Seki, H., and Minagawa, S. (1972) Equilibrium computation for the vapor growth of $\text{In}_{\text{x}}\text{Ga}_{1-\text{x}}\text{P}$ crystals, Japan. J. Appl. Phys. 11:850.

27. Kirwan, D. J. (1970) Reaction equilibria in the growth of GaAs and GaP by the chloride transport process, J. Electrochem. Soc. 117:1572.

3. RESULTS AND DISCUSSION

The value of an equilibrium analysis lies in its ability to explain the experimental results and be able to predict the composition of the prepared ternaries from the starting concentrations of the reactants. Inherent in these criteria is the ability to find phenomena that will extend the usefulness of the VPE-hydride-alloy system. The present analysis fulfills these objectives.

A number of investigators^{14, 17, 23} have studied the VPE-hydride technique using an alloy source to prepare $\text{In}_x\text{Ga}_{1-x}\text{As}$. Kordos et al¹⁷ and Jacobs et al²³ reported the compositions of the ternaries obtained as a function of the alloy compositions at fixed partial pressures of hydrogen chloride and arsine. The results of these studies are shown in Figures 1 and 2 along with the curves calculated using the same values for the parameters as those of the investigators. Figures 1 and 2 depict the excellent agreement between theory and experiment even though the variables differed markedly between the two studies. The values of $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}^*$ used were assumed to remain constant at the different deposition temperatures in these equilibrium calculations. Although $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}^*$ should vary with temperature, the results indicated that the assumption was tenable. Calculations using the experimental data of Chatterjee et al¹⁴ and Quinlan et al¹⁶ for the preparation of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ gave values for the mole fraction of InAs in the ternary of 0.62 and 0.57, respectively. The atomic % gallium in the alloys used by Chatterjee et al¹⁴ and Quinlan et al¹⁶ were 3.2 and 11.8, respectively. Although the calculations using the data of Erstfeld et al¹⁵ did not give acceptable agreement, the data did show the need of a high partial pressure of $\text{HCl}(2.3 \times 10^{-3} \text{ atm})$ to prepare $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ when the alloy composition was 12 atomic % gallium. This result is in agreement with the value found by Quinlan et al.¹⁶ The agreement of the present equilibrium method with the various experimental data clearly indicates its general applicability.

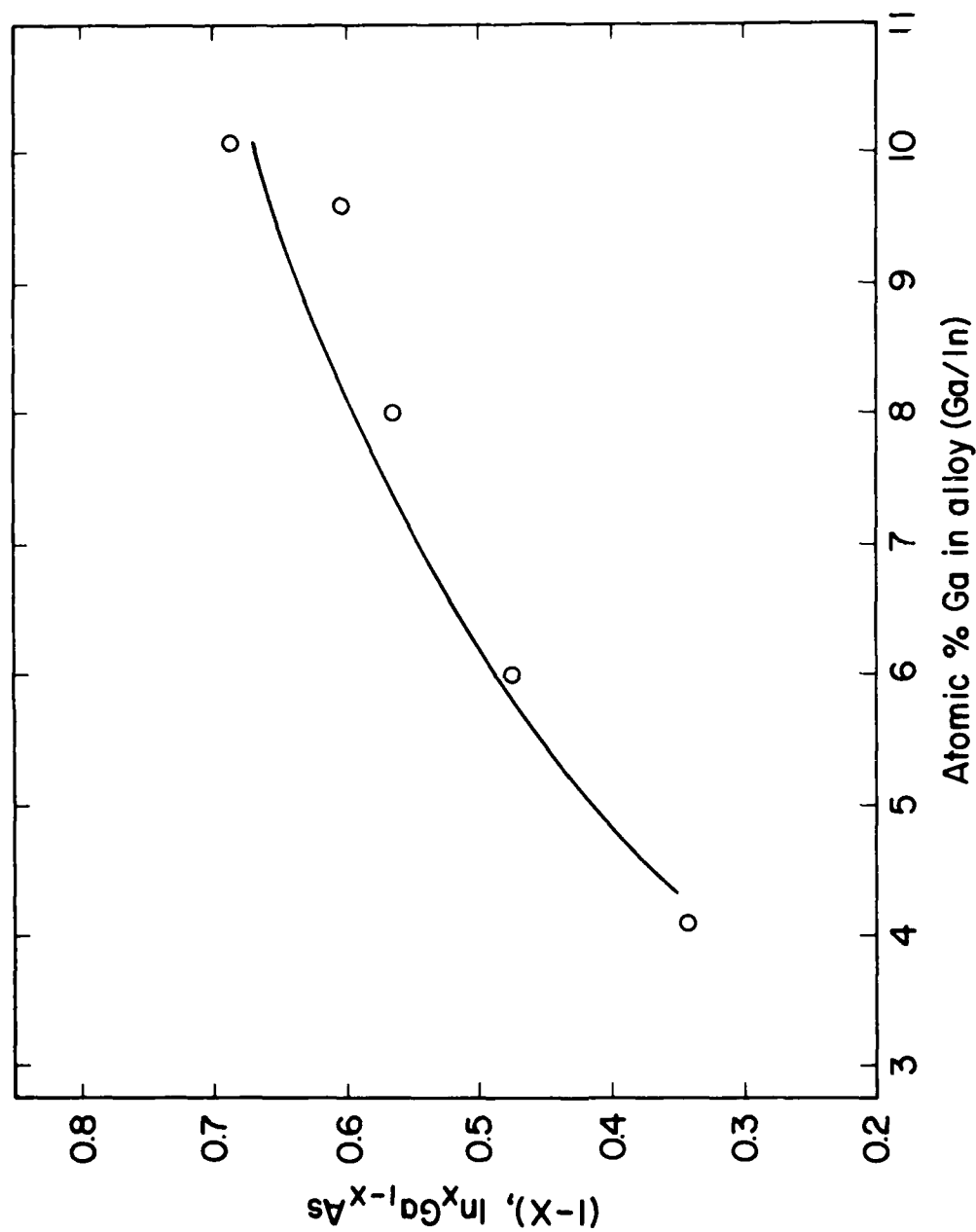


Figure 1. Mole Fraction of GaAs, $1-x$, in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of the Atomic % Gallium in the Gallium-Indium Alloy Source: (—), Calculated by the Present Method; (o), Experimental Data of Jacobs, Bugge, and Simons.

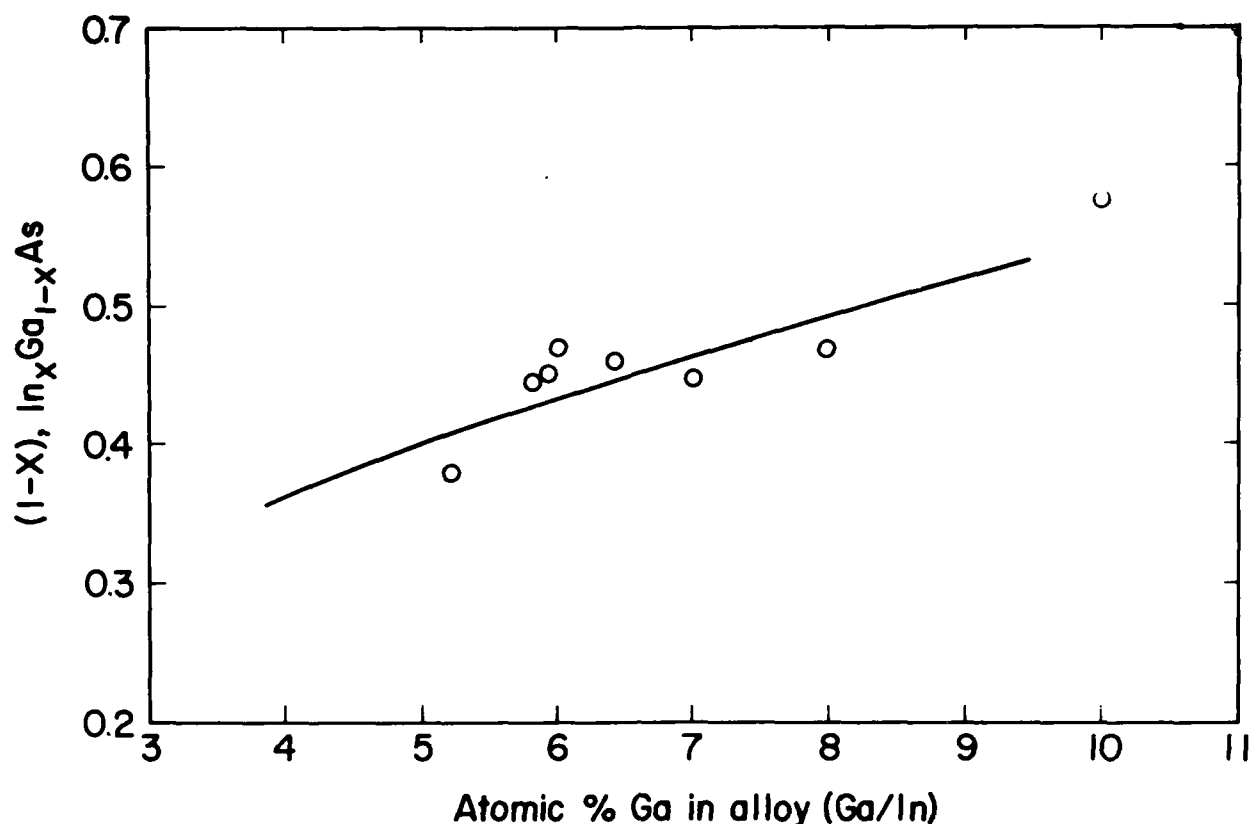


Figure 2. Mole Fraction of GaAs, $1-x$, in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of the Atomic % Gallium in the Gallium-Indium Alloy Source: (—), Calculated by the Present Method; (o), Experimental Data of Kordos, Schumbera, Heyen and Balk¹⁷

The equilibrium analysis was extended to study the systematic effect of varying the initial partial pressure of hydrogen chloride with various alloys on the composition of the $\text{In}_x\text{Ga}_{1-x}\text{As}$. Figure 3 shows the variation of the mole fraction of gallium arsenide in the ternaries as a function of the partial pressure of hydrogen chloride at four alloy compositions. The curves were calculated at a deposition temperature of 675°C and at an arsenic pressure ($P_{\text{As}_4}^\circ$) of 2.5×10^{-3} atm. The mole fraction of the GaAs is calculated only in the 0.4 to 0.6 range since the analysis method has been shown to be valid in this range. The figure shows that the gallium arsenide concentrations in the ternaries are increased with increasing partial pressures of HCl at each alloy composition. Greater changes in the partial pressures of hydrogen chloride are required to effect a change in the composition of the ternary with alloys containing less gallium than those with greater amounts. These results suggest that the preparation of a lattice matched $\text{In}_x\text{Ga}_{1-x}\text{As}$ would require less control of the HCl with an alloy containing smaller amounts of gallium.

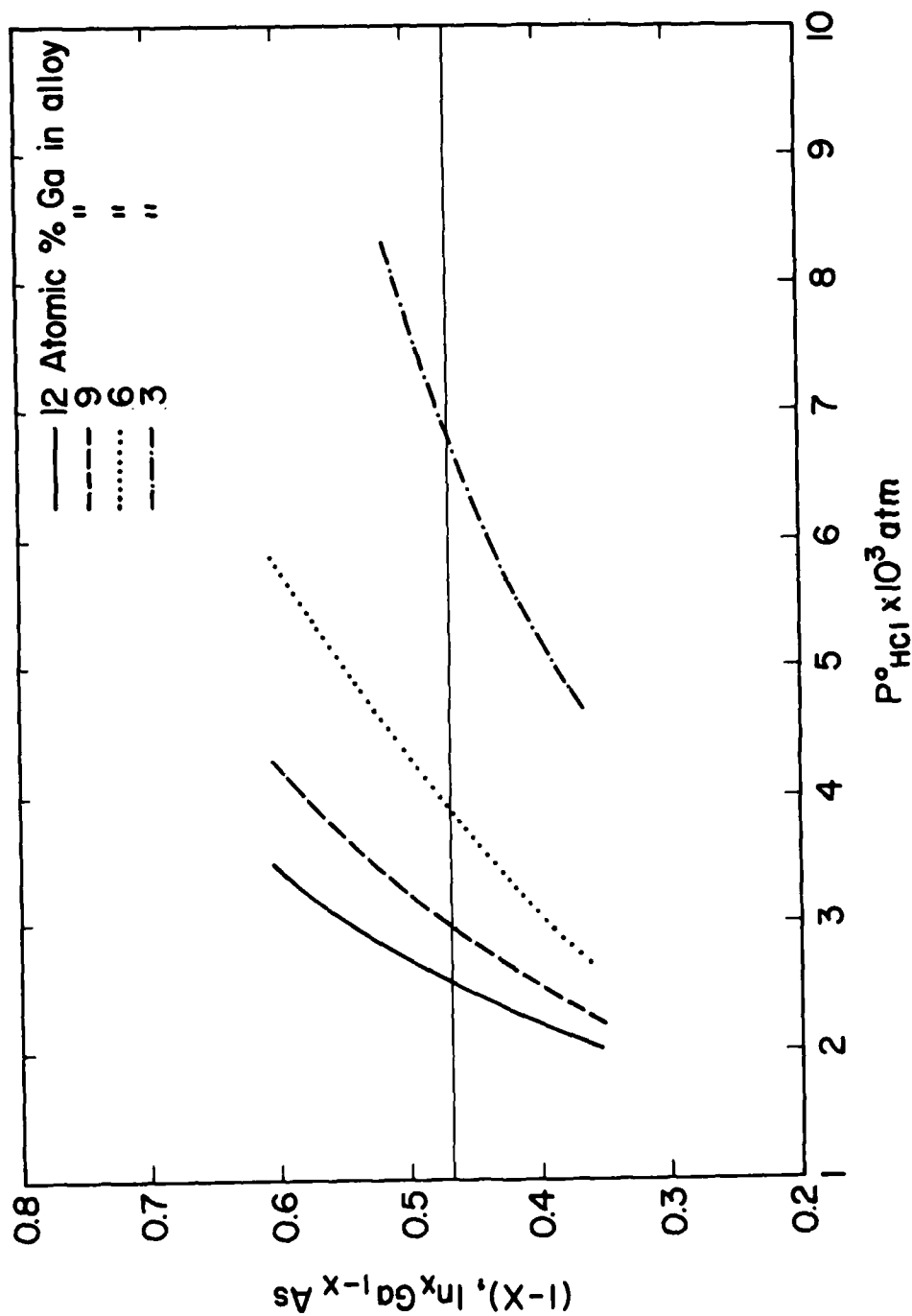


Figure 3. Calculated Mole Fractions of GaAs, $1-x$, in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of the Initial Partial Pressures of Hydrogen Chloride (P_{HCl}^0) at Various Alloy (Ga/In) Source Compositions. Curves calculated at $P_{\text{As}_4}^0 = 2.5 \times 10^{-3} \text{ atm}$ ($P_{\text{InGa}_{1-x}\text{As}}^* = 3.2 \times 10^{-4} \text{ atm}$), source temperature (T_S) = 800°C , and deposition temperature (T_D) = 675°C .

Alloys with high concentration of gallium requires smaller partial pressures of HCl to produce a desired ternary, for example, a 12 atomic % gallium alloy requires 2.5×10^{-3} atm of HCl to prepare $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ while a 3 atomic % Ga alloy requires 6.7×10^{-3} atm. These calculated trends exemplified in Figure 3 are validated from the experimental data of the various investigators presented in the previous paragraph, for example, the trend of requiring less HCl with alloys containing higher amounts of gallium to prepare $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ agrees with the experimental results of Kordos et al.¹⁷ and Quinlan et al.¹⁶ Kordos et al found that a partial pressure of 5×10^{-3} atm for HCl was necessary to prepare $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with a 7 atomic % gallium alloy while Quinlan et al reported a value of 2.3×10^{-3} atm for HCl with a 11.8 atomic % alloy. The same initial partial pressure of arsine was used in both studies.

Previously, investigators studying the VPE-hydride-alloy system to prepare $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ varied the alloy composition while keeping the initial partial pressure of $\text{HCl}(P_{\text{HCl}}^{\circ})$ constant. Figure 3 demonstrates that $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ can be prepared from the various alloys by utilizing the P_{HCl}° corresponding to this ternary. A plot of the initial partial pressures of $\text{HCl}(P_{\text{HCl}}^{\circ})$ required to form $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ at various alloy compositions is depicted in Figure 4. Experimental studies^{14, 15} on the preparation of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with the same alloy showed that the gallium content of the alloy decreases with continuous operation. Inspection of Figure 4 illustrates the fact that $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ can be prepared continuously from the same alloy even though the gallium concentration is decreasing. The decrease of the gallium concentration in the alloy can be compensated by increasing the P_{HCl}° which increases the mole fraction of GaAs in the ternary. This approach alleviates the problem of replacing the gallium in the alloy when a constant P_{HCl}° is used.

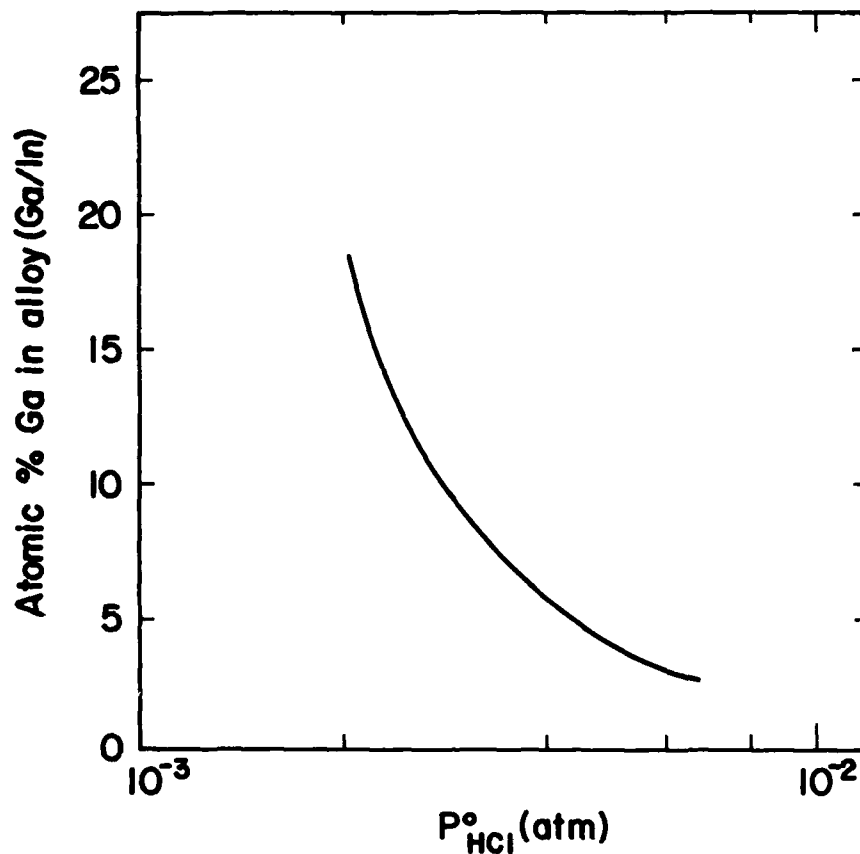


Figure 4. Calculated Initial Partial Pressures of Hydrogen Chloride (P_{HCl}^0) Required for the Preparation of $In_{0.53}Ga_{0.47}As$ at Various Alloy (Ga/In) Source Compositions. Curves calculated at $P_{As_4}^0 = 2.5 \times 10^{-3}$ atm ($P_{In_xGa_{1-x}As}^* = 3.2 \times 10^{-4}$ atm), source temperature (T_S) = $800^\circ C$, and deposition temperature (T_D) = $675^\circ C$

The effect of varying the partial pressure of arsenic ($P_{As_4}^0$) on the composition of the ternary was explored. Figure 5 demonstrates that increases in $P_{As_4}^0$ to a value of 1.0×10^{-3} atm increases the amount of indium arsenide being deposited in the ternary. Weyburne et al.²⁸ and Kajiyama²⁰ observed similar results in their

28. Weyburne, D.W., and Quinlan, K.P. (1985) The Effects of Arsine Pressure on the Compositions, Carrier Concentrations, Mobilities and Growth Rates of Epitaxial Layers of $Ga_{1-x}In_xAs$ Prepared by the VPE-Hydride Technique, Report No. RADC-TR-85-238, ADA 165278, Rome Air Development Center, Air Force Systems Command, Griffiss Air Force Base, NY.

experimental studies with the separate metals arrangement and the alloy system, respectively. The indium arsenide mole fraction remains constant with further increases in $P_{As_4}^\circ$ beyond 1.0×10^3 atm. The equilibrium analysis studies of Jacobs et al.²² and Kajiyama²⁰ demonstrated that the InAs mole fraction remains constant at high $P_{As_4}^\circ$ while Nagai²¹ reported a continuous increase. The present analysis also shows that the amount of indium deposited at low $P_{As_4}^\circ$ values is a function of the ratio of the initial partial pressure of indium monochloride to the total III monochlorides ($P_{InCl}^\circ / (P_{InCl}^\circ + P_{GaCl}^\circ)$). This dependency of the indium incorporation on ($P_{InCl}^\circ / (P_{InCl}^\circ + P_{GaCl}^\circ)$) is probably related to the increase in number of effective collisions between the As_4 molecules and the indium species with increasing $P_{As_4}^\circ$.

4. CONCLUDING REMARKS

The equilibrium analysis presented demonstrates good agreement between the calculated values and those determined experimentally. The analysis shows that the composition of the deposited ternary, $In_xGa_{1-x}As$, is dependent on the various variables, for example, P_{HCl}° 's, $P_{As_4}^\circ$'s, and alloy compositions. Studies with the equilibrium method indicates that VPE-hydride technique with the alloy source can be used continuously to prepare $In_{0.53}Ga_{0.47}As$.

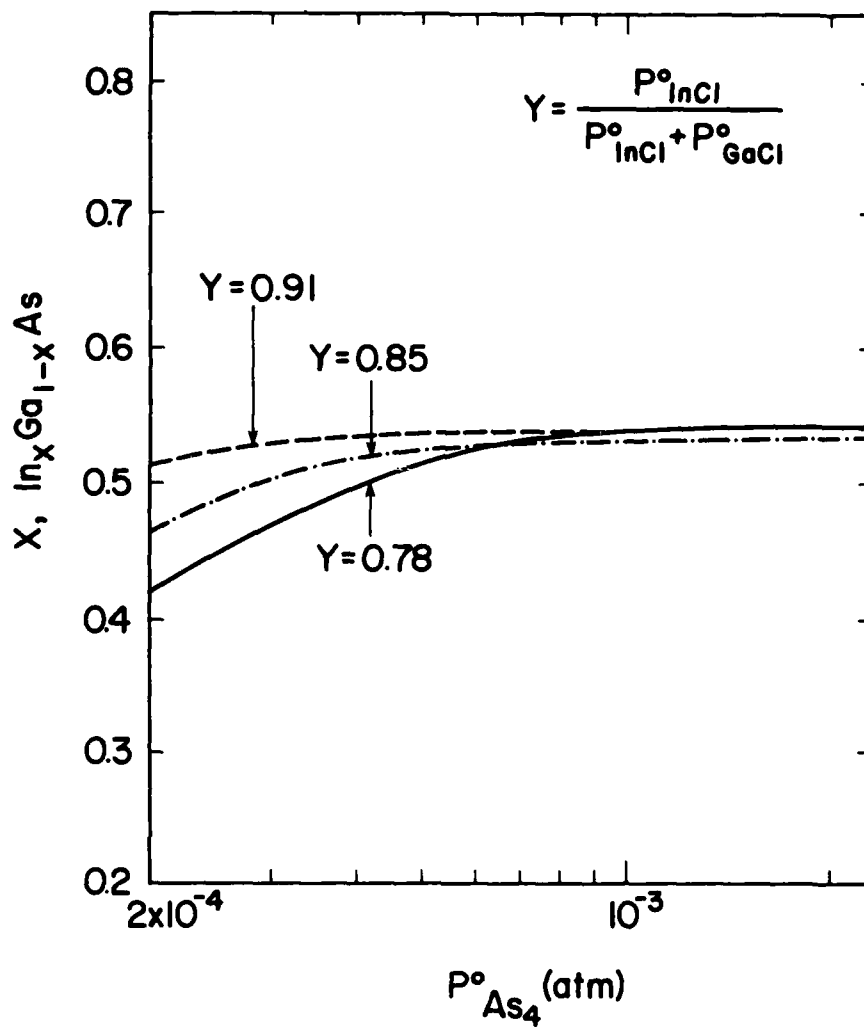


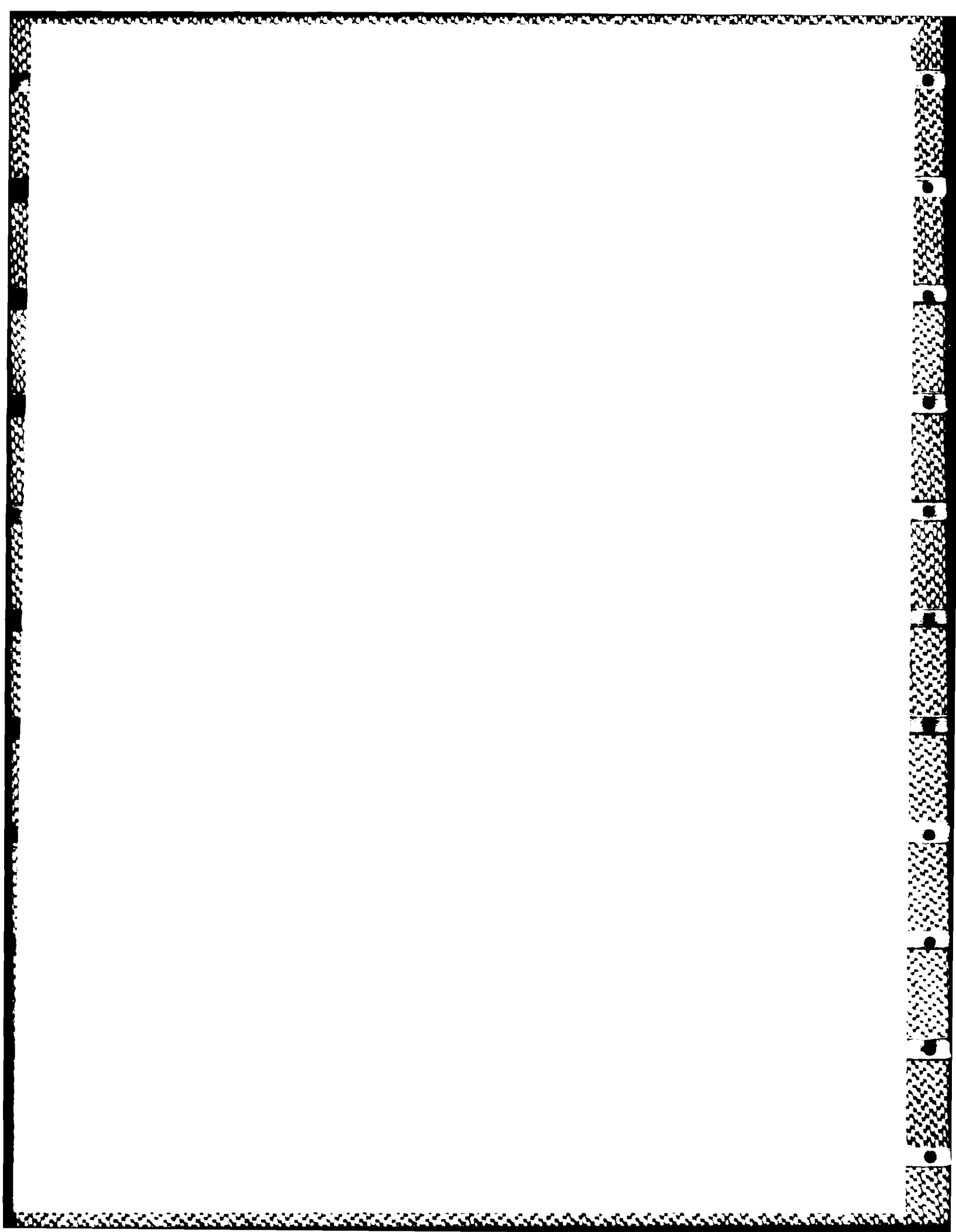
Figure 5. Variation of InAs Mole Fraction, x , in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of

$P_{\text{As}_4}^{°}$ at Different Y Values, $Y = \frac{P_{\text{InCl}}^{°}}{P_{\text{GaCl}}^{°} + P_{\text{InCl}}^{°}}$ • $Y = 0.91$: alloy source,

$\text{Ga/In} = 7 \text{ atomic \%}/93 \text{ atomic \%}$, $P_{\text{HCl}}^{°} = 8.2 \times 10^{-3} \text{ atm}$. $Y = 0.85$: alloy source,

$\text{Ga/In} = 12 \text{ atomic \%}/88 \text{ atomic \%}$, $P_{\text{HCl}}^{°} = 6.0 \times 10^{-3} \text{ atm}$. $Y = 0.78$: alloy source,

$\text{Ga/In} = 18 \text{ atomic \%}/82 \text{ atomic \%}$, $P_{\text{HCl}}^{°} = 4.9 \times 10^{-3} \text{ atm}$. Source temperature (T_S) = 800°C , and deposition temperature (T_D) = 700°C



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